VI.6 Highly Textured Glass Composite Seals for Intermediate-Temperature SOFCs

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Objectives

- Fabricate a compliant seal that is hermetic at solid oxide fuel cell (SOFC) operating conditions.
- Achieve target leak rates with minimum compressive loading.
- Identify a glass composition that is chemically compatible with a metal interconnect and does not support chromium migration or silicon degradation.

Approach

- Design a textured composite seal consisting of a glass matrix and a crystalline particulate filler.
- Optimize composite seal composition by characterization and leak rate testing.
- Analyze each composition and tailor seal to meet Solid State Energy Conversion Alliance (SECA) SOFC requirements.

Accomplishments

- Fabricated pure glass seals that demonstrate a leak rate of $8.55E^{-4}$ sccm/cm from 650-850°C at 7.9 psi.
- Downselected composite design structure and two glass compositions.
- Demonstrated composite design seals that achieve a leak rate of $1.55E^{-1}$ sccm/cm from 650-850°C at 80 psi.

Future Directions

- Optimize composite seal composition.
- Conduct lifetime leak testing.
- Scale up to full SOFC seal testing at open circuit voltage (OCV).

Introduction

To achieve the high power densities promised by planar stacks in solid oxide fuel cells (SOFCs), reliable seal technology must be developed. Current seal technology has been successful in laboratory stack testing, but in practice is plagued by reliability and lifetime issues, particularly with respect to thermal cycling. Current seal materials are dependent upon glass and glass-ceramic technologies with significant alkali, borate, and phosphate contents, constituents that are known to be highly mobile at cell operating temperatures. The volatilization of these species can degrade cell performance and ultimately limit cell life. Many of the reported seal formulations have been designed to operate near 1000°C using ceramic interconnect materials, rather than the 600-800°C range, where the use of metallic interconnects is envisioned. A composite approach, in which a crystalline ceramic phase is oriented in a compliant glass matrix, achieves good thermal, mechanical, and chemical stability through the stress relief and self-healing character of the viscous seal material and the interlocking nature of the crystalline phase.

Approach

By adding a crystalline component to a glass matrix, the seal can adhere while staying thermally and mechanically compliant. The crystalline particulates restrict flow of the glass and maintain the coefficient of thermal expansion (CTE) of the seal in the same range as other common SOFC materials. Composite seals are adaptable to either compressive or non-compressive SOFC designs. These seals adhere to metallic interconnects and are designed to avoid barium chromate formation in contact with the seals and limit silica migration to the anode by limiting the glass content of the seals.

Results

Many different glass compositions were characterized and leak tested. A study was performed in parallel to optimize the design of the composite seal, which consisted of a glass matrix and a crystalline particulate filler. Textured alumina platelets and untextured zirconia particulates were investigated as the filler material. A single glass composition was selected to simplify processing and optimize the glass content of the composite seal. Increasing the surface area of the starting glass powder from 3.7 to 15 m^2/g was found to improve its wetting behavior. Slurry containing glass powder and filler material suspended in an organic solvent was tape cast, dried, laminated, and cut to the desired sample configuration. Painting the surfaces of the sample with glass ink or laminating a pure glass tape layer on the seal surface increased the adherence of the seal, and in turn resulted in lower leak rates.

The seal leak testing conditions also were optimized. The interconnect manifolds originally were fabricated from Inconel stock material (CTE $15.8E^{-6}$/°C), and the CTE mismatch with glass compositions (typically ~$6E^{-6}$/°C) was deemed too large for the glass-interconnect interface. The Inconel manifolds were replaced with Crofer 22 APU (CTE $12.6E^{-6}$/°C), which was an improvement, although still a significant difference in CTE. Therefore, the initial heating ramp rate of the test was decreased from 10 to 3°C/min to further ease the CTE mismatch between the sealing interfaces. A mechanical load of 80 psi was established, which is lower than those used by other seal research groups (1,2). At the start of the test, the temperature of the test rig was increased to 850°C and held for one hour to allow the glass to soften and adhere to the interfaces. After measuring the sample leak rate at 850°C with helium gas, the temperature was decreased 50°C and the sample was tested again after the temperature had equilibrated. This procedure was repeated until the leak rate was tested at 850°C, 800°C, 750°C, 700°C, and 650°C.

Figure 1 summarizes testing to date on the textured alumina platelet composite. Pure glass and pure alumina tested under the same conditions are shown for reference. Composite A has an average leak rate of $1.55E^{-1}$ sccm/cm from 650-850°C, which is near our target of $1.0E^{-1}$ sccm/cm. This contrasts with a pure alumina particulate leak rate of 4.19 sccm/cm and a pure glass seal leak rate of $7.57E^{-2}$ sccm/cm. In future testing, the optimized composite seal will be examined under typical SOFC operating conditions at OCV. The new test configuration monitors OCV and degradation of the cell. This test will determine the adherence of the seal to current NexTech Materials, Ltd. SOFC materials and

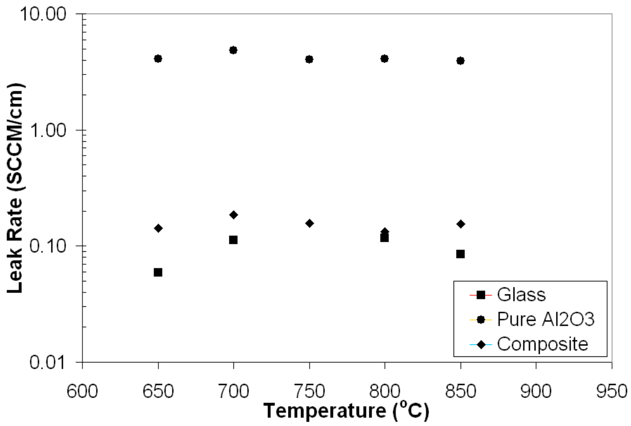

Figure 1. Alumina Composite Seal Leak Behavior at 80 psi Mechanical Loading

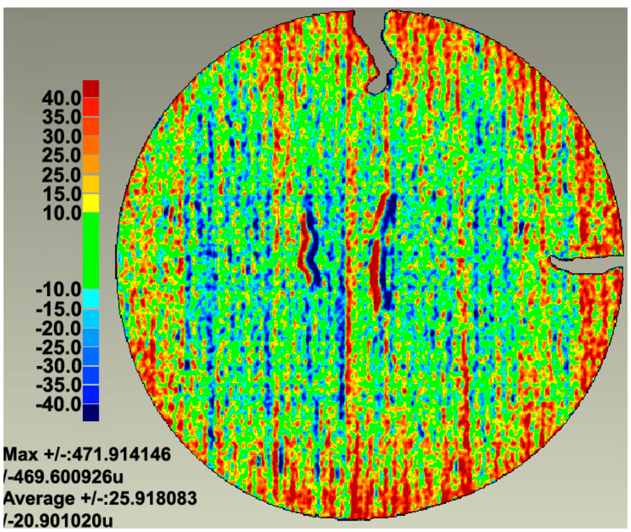

Figure 2. Observed Curvature Change at 556°C of E-Brite Joined to Glass

measure leak rates using a nitrogen/hydrogen gas mixture or air.

Ohio State University is currently characterizing the joining of glass to common SOFC components (YSZ, LSM, Inconel, E-Brite, Crofer, NiO) and scanning the samples by optical profilometry to detect curvature changes. Researchers are also using laser dilatometry on stacks integrated with glass seals to analyze CTE changes. In addition, they are analyzing the interfaces using scanning electron microscopy, energy-dispersive x-ray spectroscopy, and x-ray diffraction to detect phase changes due to chromate formation and mobilization. Figure 2 shows observed curvature changes (relative to room temperature) at 556°C in E-Brite joined to glass. Green indicates no change in curvature, red denotes an increase in curvature, and blue signifies a decrease in z-height. Areas in which no sample appears to be present constitute areas of dropout and can be ignored. Initial investigations gave no indication of a third phase, implying that no reaction has taken place between the materials. Also, curvature change of Crofer is minimal after joining to glass at 850°C.

Conclusions

- Fabricated pure glass seals that demonstrate a leak rate of $8.55E^{-4}$ sccm/cm from 650-850°C at 7.9 psi.
- Downselected composite design structure and two glass compositions.
- Converted manifolds to Crofer 22 APU to ease CTE mismatch.
- Demonstrated composite design seals that achieve a leak rate of $1.55E^{-1}$ sccm/cm from 650-850°C at 80 psi.

Special Recognitions & Awards/Patents Issued

1. Best Commercial Presentation, "Composite Seals for Intermediate Temperature SOFCs," ASM International Conference on Joining of Advanced and Specialty Materials VII, October 18-20, 2004, Columbus, OH.

FY 2005 Publications/Presentations

1. "Composite Seals for Intermediate Temperature SOFCs," ASM International Conference on Joining of Advanced and Specialty Materials VII, October 18-20, 2004, Columbus, OH.

References

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2. "Deformation behavior and leakage tests of alternate sealing materials for SOFC stacks," Bram M., Reckers S., Drinovac P., Monch J., Buchkremer P., Stover D. *Journal of Power Sources*. 138 (2004) 111-119.